BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL USING ZEOLITE AS CATALYST : EFFECT OF HEXANE IN SOLVENT EXTRACTION OF RUBBER SEED

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ABSTRACT

Petrol is the most demanding fuel nowadays. Petrol is used especially as a fuel for cars, aircraft and other vehicles. The declining petroleum source that we face today causes the increasing of the petroleum prices all over the world. This problem can be solved by using an alternative source to replace the usual commercial petrol we are using now. This can be done by producing biopetrol or biofuel. Currently, most of the bio-petrol is produced from oils such as the utilization of palm oil for the production of more environmental friendly bio-fuels. . The objective of this study is to synthesize biopetrol from fatty acid in rubber seed oil via catalytic cracking using zeolite as catalyst. Extracting rubber seed oil from the rubber seeds, is a favorable method as rubber seed oil contains more fatty acid to be produced into bio-petrol. The rubber seeds are readily available in our country for ages, cheap and help to improve the socioeconomic issues. The rubber seed oil is extracted using the Soxhlet Extraction method. The cleaned, shelled and milled rubber seeds are placed into a thimble in the main chamber of the extractor. The solvent, hexane in the receiving flask is left to boil until it vaporizes and condenses filling up the main chamber, extracting the rubber seed oil from the rubber seeds. The catalytic cracking of the mixture of 0.1L of rubber seed oil, 20g of catalyst which is in this case zeolite and anti-bumping granule(to assist well distributed boiling) at 300^{0}C for 45 minutes is to boost up the rate of reaction so that more successful reactions between the reactant particles can occur. The presence of Isooctane in a sample detected using Gas Chromatogram indicating that bio-petrol can be produced. Standards of different ratio mixtures of hexane and Isooctane were used to obtain chromatograms for Isooctane until a calibration curve is plotted from which the Isooctane produced can be determined. The results show that the actual concentration of Isooctane is very high. This could be explained using the cause of interlayer spacing of catalyst structure, larger surface area for reactions to occur, various types of fatty acid mixture present in rubber seed oil, the incorrect chromatogram modifications and also the contamination in rubber seed oil. The volume of solvent used will affect the percentage of concentration of Isooctane in samples obtained. As a conclusion, bio-petrol can be produced from rubber seed oil using zeolite catalyst in the catalytic cracking process.

ABSTRAK

Petrol adalah bahan api yang paling banyak diperlukan pada masa kini. Petrol digunakan sebagai bahan api kenderaan. Kemerosotan sumber petrol pada masa kini menyebabkan harga petrol terus meningkat di seluruh dunia. Masalah ini dapat diselesaikan dengan adanya satu sumber alternatif untuk menggantikan petrol komersial biasa. Ini boleh dilakukan dengan menghasilkan biopetrol. Pada masa kini kebanyakkan biopetrol dihasilkan daripada minyak sawit untuk menhasilkan biopetrol yang mesra alam. Objektif kajian ini adalah untuk menghasilkan biopetrol daripada asid lemak daripada biji getah melaui kaedah pemecahan asid lemak berpemangkin dengan zeolite sebagai pemangkin. Pengekstrakkan minyak getah daripada biji getah adalah cara yang efektif disebabkan biji getah mengandungi lebih banyak asid lemak yang dapat ditukarkan kepada biopetrol.biji getah boleh didapati dengan senang di Negara kita sejak dulu , murah, dan bantu memperbaiki isu sosio ekonomi. Minyak biji getah diekstrak mengunakan pengekstak soklet. Biji getah dibersihkan, dikuliti, dan dikisar. Kemudian diisikan ke dalam bidal dan disimpan kedalam pengekstrak soxhlet. Pelarut iaitu heksana dibenarkan mendidih di bekas menerima di bawah sekali sehingga ianya menyejat dan seterusnya mengkondensasi di bahagian utama di atas dengan seterusnya mengekstrak minyak biji getah daripada biji getah. Seterusnya pemecahan berpemangkin 0.1 liter minyak biji getah dengan 20 gram pemangkin iaitu zeolite dilakukan pada suhu 300^{0}C selama 45 minit untuk meningkatkan lagitindak balas antara bahan tindak balas. Kehadiran isooctan dalam dalam bahan sample ditentukan dengan mengunakan kromatogram gas untuk membuktikan kehadiran biopetrol. Sample dengan beza kepekatan campuran heksana dan isooctane digunakan untuk mendapatkan kromatogram sehingga penuntukuran garis tepat diperolehi. Keputusan akhir menunjukkkan kepekatan akhir isooktane sebenarnya agak tinggi. Ini boleh dijelaskan mengunakan teori bentok permukaan pemangkin dan luas permukaan yang didapati untuk tindak balas, pelbagai jenis asid lemak yang dapat diperolehi dalam biji getah, ralat pada kromatogram gas, dan benda asing dalam minyak biji getah. Akhirnya didapati jumlah pelarut yang digunakan mempengaruhi jumlah isooktan yang diperolehi. Kesimpulannya biopetrol dapat dihasilkan mengunakan zeolite sebagai pemangkin dalam proses pemecahan berpemangkin dengan berjayanya.

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P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
m	-	Meter
n	-	Number of moles
L	-	Liter

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CHAPTER 1

1.0 INTRODUCTION.

1.1 History Of Biofuel

Bio-fuels seem to be hot topic in today's energy markets, so what's the scoop? First of all, biofuels come in many varieties, but in general, there are two main products, those that replace (or blend with) gasoline, and those that replace (or are blended with) middle distillate fuels, such as diesel fuel, or home heating oil. For gasoline replacement and blending, the predominant fuel is ethanol, which is a water-clear liquid that is distilled from a variety of plants, but most commonly corn in the US. Distillate fuel substitutes can also be derived from a variety of plants such as soybeans, palm seeds, and peanuts, or even animal by-products such as used cooking oil grease. Resulting fuel is usually referred to as Biodiesel or B100 (100% Biofuel, no petroleum). When used as a heating oil blend, the product is sometimes referred to as Bioheat. When oils derived from these sources start out, they are not suitable for combustion, or use in a diesel engine, they need to be processed first. The process for converting raw fats and oils into "Biodiesel" separates the oil from the glycerin (one of the main components of soap). Once the glycerin is removed, the resulting Biodiesel can be used virtually interchangeably with diesel fuel or home heating oil. One important benefit of these fuels is that they have similar energy value per gallon as conventional heating oil, with the added benefits of the clean burning Biofuel.

Biofuels in the solid form has been in use ever since man discovered fire. Wood was the first form of biofuel that was used even by the ancient people for cooking and heating. With the discovery of electricity, man discovered another way of utilizing the biofuel. Biofuel had been used since a very long time for the production of electricity. This form of fuel was discovered even before the discovery of the fossil fuels, but with the exploration of the fossil fuel like gas, coal, and oil the production and use of biofuel suffered a severe impact. With the advantages placed by the fossil fuels they gained a lot of popularity especially in the developed countries. Liquid biofuel have been used in the automotive industry since its inception.

One of the first inventors to convince the people of the use of ethanol was a German named Nikolaus August Otto. Rudolf Diesel is the German inventor of the diesel engine. He designed his diesel engine to run in peanut oil and later Henry Ford designed the Model T car which was produced from 1903 to 1926. This car was completely designed to use hemp derived biofuel as fuel. However, with the exploration of huge supplies of crude oil some of the parts of Texas and Pennsylvania petroleum became very cheap and thus lead to the reduction of the use of biofuels. Most of the vehicles like trucks and cars began using this form of fuel which was much cheaper and efficient.

In the period of World War II, the high demand of biofuels was due to the increased use as an alternative for imported fuel. In this period, Germany was one of the countries that underwent a serious shortage of fuel. It was during this period that various other inventions took place like the use of gasoline along with alcohol that was derived from potatoes. Britain was the second country which came up with the concept of grain alcohol mixed with petrol. The wars frames were the periods when the various major technological changes took place but, during the period of peace, cheap oil from the gulf countries as well as the Middle East again eased off the pressure.

With the increased supply the geopolitical and economic interest in biofuel faded away. A serious fuel crisis again hit the various countries during the period of 1973 and 1979, because of the geopolitical conflict. Thus (OPEC), organization of the petroleum

Exporting countries made a heavy cut in exports especially to the non OPEC nations. The constant shortage of fuel attracted the attention of the various academics and governments to the issues of energy crisis and the use of biofuels. The twentieth century came with the attention of the people towards the use of biofuels. Some of the main reasons for the people shifting their interest to biofuels were the rising prices of oil, emission of the greenhouse gases and interest like rural development. (biofuel.org.uk)

Bio-fuels are better for the environment mainly because they contain no sulfur. When a fuel containing sulfur is burned, sulfur dioxide SO2 is produced, which is a harmful gas that has been known to cause acid rain. Although the petroleum portion of the fuel still contains sulfur, the bio portion does not. Biofuels also reduce NOX emissions, which are greenhouse gasses. There are also many indirect environmental benefits of bio-fuels. For instance, the crops grown to produce bio-fuels such as soybeans consume a great deal of CO2, which is a greenhouse gas. Biodiesel (B100) is also non-toxic, biodegradable, and environmentally benign if spilled.

1.2 Research Background.

Biofuel production as a renewable source are renewable, efficient, and clean. As petroleum becomes depleted, we grow ever more dependant on foreign sources of oil, often located in unstable parts of the world, and while biofuels make up only a small portion of the energy market, their role is becoming increasingly more vital every day. t Soaring prices of fossil fuels, geo-political issues and environmental pollution associated with fossil fuel use has led to worldwide interest in the production and use of bio-fuels. Both the developed and developing countries have developed a range of policies to encourage production of combustible fuels from plants that triggered public and private investments in bio-fuel crop research and development, and bio-fuels production. In this article, we discuss the potential benefits of bio-fuels in increasing the farmers' incomes, reducing environment pollution, the crop options and research and development interventions required to generate feed stocks to produce bio-fuels to meet projected demand without compromising food/fodder security in developing countries. Producing petrol from the waste of palm oil (palmitic acid) will give an alternative choice to the users, especially for petrol engine vehicles' owners. In addition, this bio petrol, which is graded 100 for its octane number, burns very smoothly so bio petrol can reduce emissions of 2some pollutants. Research is currently being developed by teams of the of Chemical Engineering in Universiti Teknologi Petronas, (UTP) on the synthesize of biofuel from rubber seeds in Malaysia. It states that rubber-seed oil has high content of free fatty acids (FFAs). Besides, there was between 30% and 40% of oil in rubber seeds and 1kg of rubber seeds could produce between 300ml and 400ml of biodiesel fuel (M.T. Azizan, 2008). The natural form of rubber seed oil is highly acidic functional groups such as carbonyl, oleifinic unsaturation, ester, glyceryl, methylene and terminal methyl are present in rubber seed oil. While, Chemical engineering lecturer Mohammad Tazli Azizan said that using rubber seeds is a bettr option because the oil in those seeds was suitable for use in cold countries, unlike palm oil. The rubber seed oil is not viscous and can be used in cold climates without much modification. There are between 30% and 40% of oil in rubber seeds.Rubber seeds were not edible but could be found in abundance in the country, adding that there were 1.2 million ha of rubber plantation in Malaysia.Using oil derived from rubber seeds instead of oil palms could easily avert the debate of a conflict between food and fuel.

1.3 Objectives

a) To synthesize Isooctane from rubber seeds
b) To analyze the concentration of Isooctane by heterogeneous catalytic cracking of fatty acid using Zeolite as catalyst.

1.4 Problem Statement

1.4.1 Peak Oil.

Peak oil is the point in time when the maximum rate of global petroleum extraction is reached, after which the rate of production enters terminal decline. This concept is based on the observed production rates of individual oil wells, and the combined production rate of a field of related oil wells. The aggregate production rate from an oil field over time usually grows exponentially until the rate peaks and then declines, sometimes rapidly until the field is depleted. This concept is derived from the Hubbert curve, and has been shown to be applicable to the sum of a nation's domestic production rate, and is similarly applied to the global rate of petroleum production. Peak oil is often confused with oil depletion; peak oil is the point of maximum production while depletion refers to a period of falling reserves and supply.

M. King Hubbert created and first used the models behind peak oil in 1956 to accurately predict that United States oil production would peak between 1965 and 1970.His logistic model, now called Hubbert peak theory, and its variants have described with reasonable accuracy the peak and decline of production from oil wells, fields, regions, and countries, and has also proved useful in other limited-resource production-domains. According to the Hubbert model, the production rate of a limited resource will follow a roughly symmetrical logistic distribution curve (sometimes incorrectly compared to a bell-shaped curve) based on the limits of exploitability and market pressures.

Some observers, such as petroleum industry experts Kenneth S. Deffeyes and Matthew Simmons, believe the high dependence of most modern industrial transport, agricultural, and industrial systems on the relative low cost and high availability of oil will cause the post-peak production decline and possible severe increases in the price of oil to have negative implications for theglobal economy. Predictions vary greatly as to what exactly these negative effects would be. If political and economic changes only occur in reaction to high prices and shortages rather than in reaction to the threat of a peak, then the degree of economic damage to importing countries will largely depend on how rapidly oil imports decline post-peak.

Optimistic estimations of peak production forecast the global decline will begin by 2020 or later, and assume major investmentsin alternatives will occur before a crisis, without requiring major changes in the lifestyle of heavily oil-consuming nations. These models show the price of oil at first escalating and then retreating as other types of fuel and energy sources are used. Pessimistic predictions of future oil production operate on the thesis that either the peak has already occurred, that oil production is on the cusp of the peak, or that it will occur shortly. The International Energy Agency (IEA) says production of conventional crude oil peaked in 2006.Throughout the first two quarters of 2008, there were signs that a global recessionwas being made worse by a series of record oil prices.

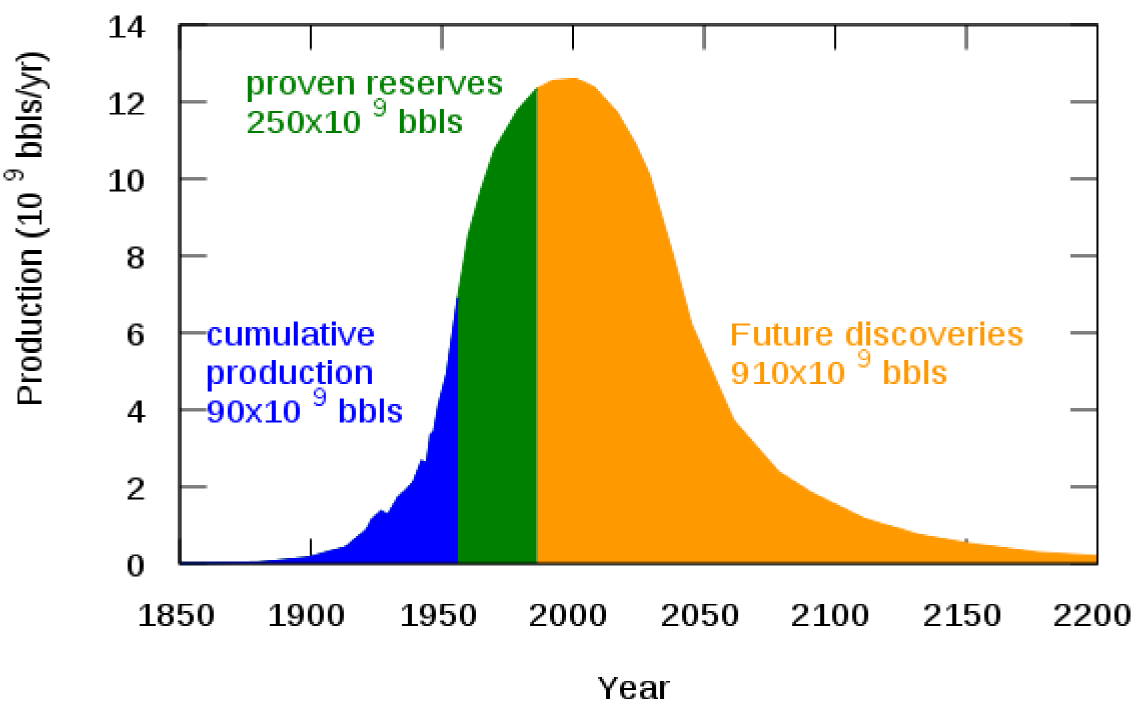

Figure 1.1: A logistic distribution shaped production curve, as originally suggested by M. King Hubbert in 1956.

1.4.2 Demand For Oil

The demand side of peak oil is concerned with the consumption over time, and the growth of this demand. World crude oil demand grew an average of 1.76% per year from 1994 to 2006, with a high of 3.4% in 2003-2004. World demand for oil is projected to increase 37% over 2006 levels by 2030 (118 million barrels per day (18.8×10^6 m^3/d) from 86 million barrels (13.7×10^6 m^3)), due in large part to increases in demand from the transportation sector.A study published in the journal Energy Policy predicted demand would surpass supply by 2015 (unless constrained by strong recession pressures caused by reduced supply).

Energy demand is distributed amongst four broad sectors: transportation, residential, commercial, and industrial. In terms of oil use, transportation is the largest sector and the one that has seen the largest growth in demand in recent decades. This growth has largely come from new demand for personal-use vehicles powered by internal combustion engines. This sector also has the highest consumption rates, accounting for approximately 68.9% of the oil used in the United States in 2006, and 55% of oil use worldwide as documented in the Hirsch report. Transportation is therefore of particular interest to those seeking to mitigate the effects of peak oil.Although demand growth is highest in the developing world, the United States is the world's largest consumer of petroleum. Between 1995 and 2005, U.S. consumption grew from 17,700,000 barrels per day (2,810,000 m^3/d) to 20,700,000 barrels per day (3,290,000 m^3/d), a 3,000,000 barrels per day (480,000 m^3/d) increase. China, by comparison, increased consumption from 3,400,000 barrels per day (541,000 m^3/d) to 7,000,000 barrels per day (1,100,000 m^3/d), an increase of 3,600,000 barrels per day (572,000 m^3/d), in the same time frame.

As countries develop, industry and higher living standards drive up energy use, most often of oil. Thriving economies such as China and India are quickly becoming large oil consumers.China has seen oil consumption grow by 8% yearly since 2002, doubling from 1996-2006. In 2008, auto sales in China were expected to grow by as much as 15-20%, resulting in part from economic growth rates of over 10% for 5 years in a row.

Although swift continued growth in China is often predicted, others predict that China's export dominated economy will not continue such growth trends due to wage and price inflation and reduced demand from the United States. India's oil imports are expected to more than triple from 2005 levels by 2020, rising to 5 million barrels per day (790×10^3 m^3/d).

The International Energy Agency estimated in January 2009 that oil demand fell in 2008 by 0.3%, and that it would fall by 0.6% in 2009. Oil consumption had not fallen for two years in a row since 1982-1983.

The Energy Information Administration (EIA) estimated that the United States' demand for petroleum-based transportation fuels fell 7.1% in 2008, which is "the steepest one-year decline since at least 1950." The agency stated that gasoline usage in the United States may have peaked in 2007, in part due to increasing interest in and mandates for use of biofuels and energy efficiency.

The EIA now expects global oil demand to increase by about 1,600,000 barrels per day (254,000 m^3/d) in 2010. Asian economies, in particular China, will lead the increase.China’s oil demand may rise more than 5% compared with a 3.7% gain in 2009, the CNPC said.

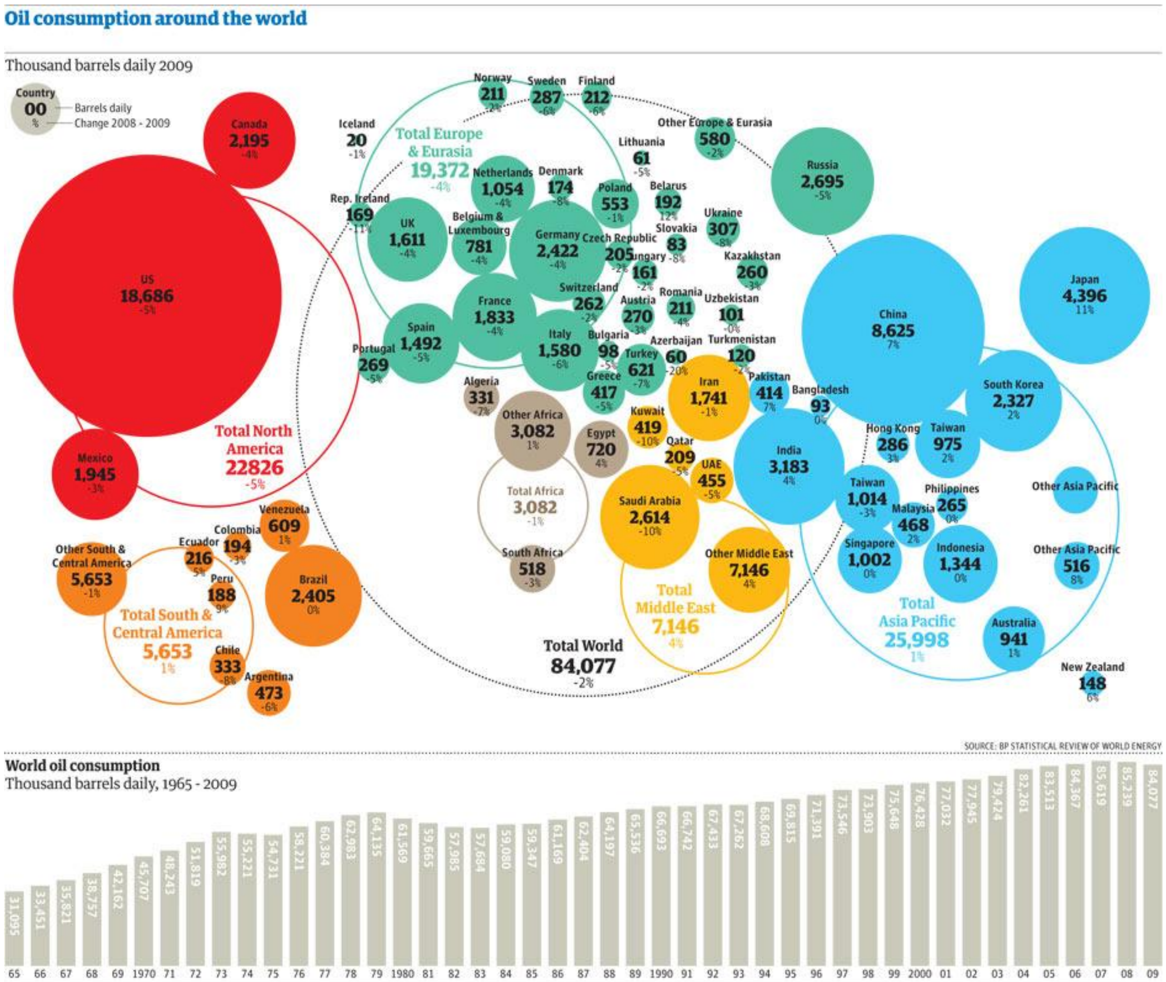

Figure 1.2: BP energy statistics: oil consumption around the world.

1.4.3 Oil Price In Malaysia And The Consequences.

The fossil fuels prices are very unstable and unpredictable. Furthermore, this price hike is estimated to be increasing for the next few more years. These changes of the prices of the fossil fuels have given a difficult time to the consumers to allocate a large sum of money to pay only for the petrol itself.

With the increasing prices of the fossil fuels, everything else indirectly will be more and more expensive. The manufacturing and transportation company will take this advantage to increase the costs. It will cause many domino effects in terms of goods and services cost as well as will affect the global economic growth and stability. Unfortunately to the consumers, the boss will never raise an increase the workers' salary. People with higher salary can still manage to pay for the price hike but for the lower income group, they will definitely feel the pinch. Bio-petrol is better than fuel from under the ground or drilled and refined fuel which is more expensive because of the cost of production. In addition, the bio-petrol is much cheaper than the fossil fuels because it is derived from biomass such as natural plants, vegetable crops like palm oil and rubber seeds as well as the agricultural or forestry waste. The process to produce bio-petrol is not as expensive as the fossil fuels. Therefore, it is believed that the bio-petrol will helps to fulfill the demand of the world in the future.

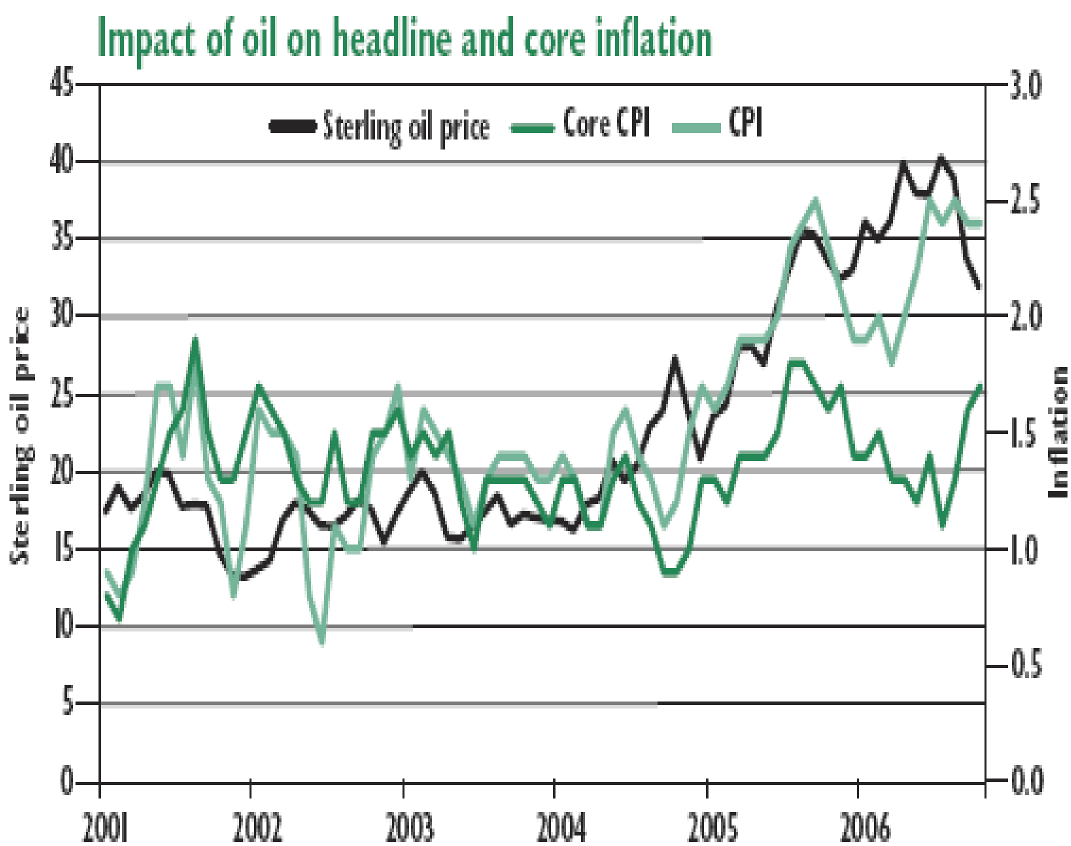

Figure 1.3: Impact of oil on headline and core inflation

1.4.4 Disadvantages Of Fossil Fuel

- Pollution is a major disadvantage of fossil fuels. This is because they give off carbon dioxide when burned thereby causing a greenhouse effect. This is also the main contributory factor to the global warming experienced by the earth today.
- Coal also produces carbon dioxide when burned compared to burning oil or gas. Additionally, it gives off sulphur dioxide, a kind of gas that creates acid rain.
- Environmentally, the mining of coal results in the destruction of wide areas of land. Mining this fossil fuel is also difficult and may endanger the lives of miners. Coal mining is considered one of the most dangerous jobs in the world.
- Power stations that utilize coal need large amounts of fuel. In other words, they not only need truckloads but trainloads of coal on a regular basis to continue operating and generating electricity. This only means that coal-fired power plants should have reserves of coal in a large area near the plant’s location.
- Use of natural gas can cause unpleasant odors and some problems especially with transportation.
- Use of crude oil causes pollution and poses environmental hazards such as oil spills when oil tankers, for instance, experience leaks or drown deep under the sea. Crude oil contains toxic chemicals which cause air pollutants when combusted.